Abstracts of the physico-chemical literature in Japan

ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

Vol. XI. APRIL, 1937 No. 2

1—GENERAL AND PHYSICAL CHEMISTRY

Light pressure and Brownian motion. M. Satô. *Sci. Repts. Tohoku Imp. Univ.* **25**, 156 (1936).—Assuming that the light pressure is caused by the elastic reflection of light quanta, the present writer calcd. the light pressure and discussed the Brownian motion of a particle in a field of radiation.

Author.

Application of transition state method to the heterogeneous reaction on hydrogen electrode. G. Okamoto, J. Horiuti, and K. Hirota. *Sci. Papers Inst. phys. Chem. Res.* **29**, 223 (1936).—The heterogeneous reaction rate was formulated statistical-mechanically, extending the transition state method. An expression was derived for the absolute rate of the catalytic atomisation or the recombination of hydrogen on a metallic catalyst. Assuming the latter process as the rate-detg. process, isotopic interchange rate, its temp., variation, isotopic sepn. factor, anodic and cathodic current were calcd. for hydrogen electrode of nickel with fair agreement with expts. Main conclusions are as follows: (i) The theory gives, after some simplification for the relation between the cathodic current i and the electrode potential η, $\log i = -\left(2-\frac{u^*}{u}\right)\frac{F\eta}{RT}$ where u is the repulsion potential between an adsorbed hydrogen atom and the surrounding ones not electronically coupled with the former, u^* that between two hydrogen atoms at the activated state and the surroundings. The potential between the two atoms being not included in u^*, we have, $u < u^* < 2u$. It follows that $0 < 2-\frac{u^*}{u} < 1$ which explains the well-known Tafel's relation. (ii) The theory tells that the catalytic atomisation rate diverges widely, according to the lattice plane on which the process takes place and that (110) plane is the most active. (iii) The catalytic atomisation (or the recombination) as the rate-detg. step for the above electrode processes is now conclusive. Author.

A note on the determination of molecular weight by ultracentrifuge. S. Oka. *Proc. Phys.-Math. Soc. Japan.* **18**, 519 (1936).–The differential equation in the case of equil. of ultracentrifuge,

$$\frac{dc}{dt}=D\left(\frac{d^2c}{dx^2}+\frac{1}{x}\frac{dc}{dx}\right)-\omega^2 s\left(x\frac{dc}{dx}+2c\right)$$

is discussed. From the boundary condition, $\omega^2 sxc - D\,dc/dx = 0$

$$\frac{C}{C_0}=\frac{\omega^2 s}{2D}\frac{x_1^2-x_0^2}{e^{\frac{\omega^2 s}{2D}x_1^2}-e^{\frac{\omega^2 s}{2D}x_0^2}}e^{\frac{\omega^2 s}{2D}x^2}$$

for the concn. results. From the condition, that this concn.-law is in agreement with the thermodynamic sedimentation equil. the Svedberg's molecular weight formula for the sedimentation velocity method is derived. For this derivation the equation f=RT/D for the coeff. of friction per mole is not used.

Author.

Kinetics of the catalysed interchange reaction $C_6H_6+HDO \rightarrow C_6H_5+H_2O$. T. Koyano. *J. Chem. Soc. Japan.* **57**, 933—935 (1936).–The rate of the catalytic interchange reaction was detd. in the presence of platinum black. The first order rate, kw, the number of gram atoms of deuterium which leave the water of 1% D content through 1 gm pt ca-

talyst by interchange, was obtained by following D content in benzene during the reaction by analysis and by the knowledge of the partion equili. It was found $kw=3\times10^{-7}$ at 50° and $kw=4\times10^{-6}$ at 100°. Activation energy of the reaction was found $-R\frac{\Delta\log kw}{\Delta\left(\frac{1}{T}\right)}=16\pm1$ Kcal. Author.

Effect of carbon dioxide on the thermal conductivity of cotten wool. Y. Takamura. *Proc. Phy.-Math. Soc. Japan.* **III,** 18, 491-496 (1936).-This study being the continuation of the previous one, the effect of Co_2 mixed in air on the thermal conductivity of cotton wool is investigated. The ratios of the conductivities $K_{t(CO_2)}$ and $K_{t(air)}$ at the same temp. are calcd. by the approximate formula $K_{t(CO_2)}/K_{t(air)}=\left(\frac{\Delta T'}{\Delta T}\right)_1\Big/\left(\frac{\Delta T'}{\Delta T}\right)_2$. The gragh of the ratio against the percentage of CO_2 is a straight line. A formula, $K_{(CO_2)}=K_{(air)}(1-0.00160y)$ is obtained, within a probable error of about 1%, in the range of density of the packing about 0.03 to 0.1, in the formula -0.00160 is the mean value of coeff. of variation of the conductivity and y the percentage of CO_2 in the air-CO_2 mixture. The rough absolute values of $K_{(CO_2)}$ are calcd. K_1 (the conductivity of the gaseous phase in the cotton wool immersed in any gas) and K_2 (that of the phase of cotton wool itself) are estimated approximately by the kinetic theory of gases under some assumptions. The result are— $K_2=4.07\times10^{-5}$, $K'_{1(air)}=1.65\times10^{-5}$, $K''_{1(H_2)}=8.36\times10^{-5}$, and $K''_{1(CO_2)}=0.85\times10^{-5}$. From the ratios K_1'/K_2 and K_1''/K_2 the following conclusion is obtained: the less the conductivity of the gas used, the more the quantity of heat passing through the phase of cotton wool becomes and the less that of heat passing through the gaseous phase. Author.

Determination of the interchange equilibrium. $C_6H_5+HDO=C_6H_5D+H_2O$. T. Koyano. *J. Chem. Soc. Japan.* **57,** 929-933 (1936).-The partition equil. was studied at 100°C, the interchange being catalysed by platinum black. The partition coeff. $k=\frac{(C_6H_5D)\ (H_2O)}{3(C_6H_6)\ (HDO)}$ was found to be 0.93. Comparing this and that obtained by Horiuti and Polanyi, (*Trans. Faraday Soc.* **30,** 1164 (1934)) k=0.95 at 200°C, it was found that the temp. coeff. of k was negligible. By ordinary statistical mech. formulation of the equil, the ratio of vibrational partition functions $Q_{C_6H_5D}/Q_{C_6H_6}$ was calcd. from k, its temp. coeff. and from spectroscopic data for H_2O and HDO to be $\frac{Q_{C_6H_5D}}{Q_{C_6H_6}}=1.7e^{\frac{h\Sigma\Delta V}{2KT}}$ where $\Sigma\Delta V=1200$ cm^{-1}. Observed difference $\Sigma\Delta V=800$ cm^{-1}, due to Ingold and others (*Nature.* **135,** 1033 (1935)) is insufficient to account for the result. Temp. independent factor 1.7 suggests that some low frequency vibrations are participated by H or D atom. Author.

Analysis by means of radioactive indicator. II. The determination of the solubility of lead chromate. M. Isibashi and O. Funakoshi. *J. Chem. Soc. Japan,* **57,** 10, 1028-1030 (1936).-In the expt. using a radioactive indicator to det. the solubility of various lead salts, difficult to be solved, the authors have first succeeded in obtaining the ext. solubility of lead chromate in water.

As a radioactive indicator they used ThB, and for measuring the activity used the radioscope made by the Rikagaku-kenkyujo. In the first place, as an exptl. material they prepared a lead acetate soln. contg. a known quantity of lead; mixed it with a certain t. of ThB, the activity of which had been measured beforehand; and got lead chromate pptd. from the mixt. Then they put the lead chromate ppt. thus prepd. into an Erlenmeyer flask contg. distilled water, and then introduced the flask into a thermostat at 25°C. and kept it shaked for 18 to 25 hrs. for the purpose of the complete saturation. After the ppt. had been filtered away, they had a known volume of the filtrate evaporated to dryness. When it cooled, they measured the activity of this residue, and then, by calcg. it back to the initial activity, gained the real amt. of the lead chromate resolved in water. The solubility of

the lead chromate in water at 25°C. thus gained in this expt. was: 6.6×10^{-5} g/L, 5.9×10^{-6} g/L, 7.7×10^{-6} g/L., 3.4×10^{-5} g/L, mean 5.8×10^{-5} g/L.$=1.8\times10^{-7}$ M/L. This value is interesting compared with those measured by former experimentalists. Author.

On measurement of deionization-time. T. Kuno and T. Sawada. *Mazda-Kenkyu-Jiho.* **11**, 2, 36 (1936).–It is important to know the deionization time of hotcathode mercury vapor rectifiers and thyratrons, because many characters of these tubes are dependent upon the time. The measuring circuit is as follows: the thyratron under test with a small inductance in the plate circuit and a capacity are connected in parallel to the direct current source through a variable resistance, and impulsive voltages are given to the grid by the other circuit. When the discharge begins the plate voltage drops suddenly to a small value and then becomes neg. by the effect of the inductance in the anode circuit, and next increases by the charging rate of the condenser by the resistance. If the resistance is decreased, the charging rate increases and at last the time is so short that positive ions in the valve can not diffuse to the grid and bulb wall well and oscillation stops. We took the oscillograms of the anode voltages, and defined the deionizatian time was the shortest time that the valve could take to gain the control power again. The results are: 1. The time decreases when the neg. grid voltages were increased. 2. The time increases when the resistance of the grid circuit were increased. 3. The time increases when the anode current increases but not remarkedly. 4. The time increases very sharply when the temp. of the mercury drops in the valve elevates, but in the case of the argon filled in tubes; the time decreases when the temp. elevates. 5. The time ranges from 100 microsec. to 1 millisec. Author.

Buffer action of the ammonium sulphate-sulphuric acid solution to the zinc sulphate solution. S. Izawa. *Mazda-Kenkyu-Jiho.* **11**, 2, 17–19 (1936).–Expts. were carried out by hydrogen electrode to det. the buffer action of H_2SO_4-$(NH_4)_2SO_4$ on $ZnSO_4$, the results were summarized as follows: (a.) Measured the effect of succesively increased addn. of H_2SO_4 on 10 cc. of $\frac{1}{2}$ M. $(NH_4)_2SO_4$ contg. no $ZnSO_4$ soln., the value of P_H successively decreased. (b.) Detd. P_H with 15 cc. of $\frac{1}{2}$-M. $(NH_4)_2SO_4$ and 10 cc. of $\frac{1}{2}$ M. $ZnSO_4$ soln. at the condition and obtained succesively decreasing values according to increasing acid. (c.) Repeated the same with 10 cc. each of the two solns., obtained almost the same results. (d.) Repeated the expts. with the 5 cc. of $\frac{1}{2}$ M. $(NH_4)_2SO_4$ soln. and 10 cc. of $\frac{1}{2}$M. $ZnSO_4$ soln., obtained the similar results. (e.) Detd. the effect of increasing addn. of acid on $ZnSO_4$ soln. only, yet obtained the similar results, but with somewhat greater rates. Author.

Chemical separation of hydrogen and oxygen isotopes. E. Ogawa. *Tech. Repts. Kyushu. Imp. Univ.* **11**, 148–151 (1936).–Formerly [*cf. Bull. Chem. Soc. Japan.* II (1936) 426, *Tech. Repts. Kyushu Imp. Univ.* II (1936)] the auther has pointed out the effect of polarisation of isotopic exchange reactions. These are the abstract of the report of the exts. on the isotopic sepn. of hydrogen and oxygen by this effect. About 1 mol. of solute was dissolved in 4000 cc. of water and water was evaporated until anhydrous salts remain. The density of the last portion of each distillate (about 30cc.) was measured.

WATER	+ 3.7	KI	+14.1
NH_4CL	+18.2	$MgCL_2$	+11.0
LiCL	+14.5	$CaCL_2$	+ 4.4
NaCL	+ 1 2	$BaCL_2$	− 0.9
KCL	+ 0.7	$CuCL_2$	+ 4.7
KF	+ 7.6	$NiCL_2$	+ 8.1
KBr	+ 6.6	$FeCL_3$	− 0.2
$CrCL_3$	− 1.5	$KAl(SO_4)_2$	+14.0
H_2SO_4	+ 4.7	NaOH	+ 8.8
$(NH_4)_2SO_4$	+11.0	KNO_3	+ 8.1
$CuSO_4$	+ 1.8	$K_3Fe(CN)_6$	+ 3.9

These isotopic shift of hydrogen and oxygen are probably attributed to solubilities of solutes, ionic mobilities, or degree of hydration of each

ion. From these results it is probably concluded that the electronic energies of isotopic mols. are not the same. This effect of polarisation surely plays very important part on the isotopic exchange reactions except hydrogen. Author.

Notes on the dose of solar ultraviolet rays. T. Takéuti and K. Inamura. *Bull. Tokyo Univ. Eng.* **5**, 610–612 (1936).–It is shown that the U. V. dosemetry gives a scale of fineness of the sky. An explanation is also proposed for the change of U. V. dose at the recent total solar eclipse.

Author.

Decomposition of hydrogen peroxide by haemin. I. H. Tominaga and G. Hazato. *J. Chem. Soc. Japan.* **57**, 1090 (1936).–Measuring the velocity of decompn. of hydrogen peroxide, (10^{-3} mol per litre) in aqueous soln. catalyzed by alkaline-haemin (10^{-5} mol per litre) prepd. from cow blood, we obtained the following empirical equations:

$$k_m = kE$$

and $$\ln kE = KC + A'$$

or $$-\frac{dC}{dt} = KEC$$

$$-\frac{dE}{dt} = k''E^2C$$

where

k_m; unimol. velocity const.
k'', k, A'; consts.
E; concn. of Haemin.
C; concn. of H_2O_2.
$k = \frac{k''}{k'}$.

These are applicable in alkaline region, with phosphate buffer (PH=6.8−7.4), and quite different from the relationship found by E. Yamasaki (*Sci. Repts. Tohoku Imp. Univ.* **9**, (1920) 13). However, in acid region (PH=6.0−6.7), the similar result as in the Yamasaki expt. was obtained, and led to the following relationships:

$$kE = k'C + A$$

or $$-\frac{dC}{dt} = kEC$$

$$-\frac{dE}{dt} = k'EC.$$

Author.

Studies on the Raman effect of organic substances. VI. Raman effect of sesquichamene and some other terpenes. K. Matuno and K. Han. *Bull. Chem. Soc. Japan.* **11**, 576 (1936).–The Raman spectra of the following substances have been studied: Sesquichamene ($C_{15}H_{24}$), *d*-sabinene, *d*-*a*-pinene, *d*-verbenol, *d,l*-*d'*-ter- pinenol-(4), menthyl acetate, and *iso*-bornyl acetate. The occurrence of the intense line at $\Delta\nu$ 1682 cm^{-1} seems to suggest that sesquichamene may have a linkage of 1–methyl cyclohexene-(1) if cedrene has a linkage of 1-metyl-cyclo-pentene (1).

Author.

The structure of molecules as revealed by dipole moment and Raman spectrum. S. Mizushima. *J. Chem. Soc. Japan.* **57**, 636 (1636).–The structure of many fundamental molecules are discussed based on the exptl. results obtained by the author and his co-workers (*Phys. Zeit.* **28** (1927), 418: **35** (1934), 905; **36** (1935) 600; *Sci. Papers Inst. Phys. Chem. Research, Tokyo*, **5** 201 (1927); **9** 209 (1928),; **25** 159 (1934); **26** 1 (1934); **29** 63, 111, 188, (1936); *Bull. Chem. Soc. Japan*, **10** (1935), 167; **11** (1936), 553, 698; etc.). The author is especially interested in the problem of the intramolecular rotation which can be studied most directly by the measurement of dipole moment and Raman spectrum, since the change of molecular symmetry caused by the intramolecular rotation brings about the change in the dipole moment as well as in the selection rule of the Raman effect. In any studies so far made the completely free rotation around a single bond is not observed, but in some cases a "frozen rotation" without an oscillatory rotation of finite amplitude. As to the intramolecular forces which give rise to the hindrance of rotation, the exchange repulsion, the electrostatic force and the disppersion attraction are taken into account. If, however, the axis of rotation possesses partially the property of a double bond by virtue of the quantum mech. resonance, the electronic effect of the bond plays the leading part in this hindrance, (e. g. phenol derivatives, carboxylic

acids and esters). For a rotation around a pure single bond C-C the mutual energy between the rotating groups is in general of the order of magnitude comparable with kT at room temp., hence the change in the intramolecular rotational state is easily effected by the change of temp. Author.

On the variation of diamagnetic susceptibility of water due to temperature. K. Honda and Y. Simizu. *Kinzoku no Kenkyu.* 13, 365–369 (1936).–The present writers tried to calc. the effect of temp. on the magnetic susceptibility of water in the following way :- The water mol. is assumed to be a neutral atom, and the electrons having a distance from the nucleus greater than the mean atomic radius are assumed to become free electrons. Then the expansion of volume caused by a rise of temp. will increase the diamagnetic susceptibility due to the increase of bound electrons at the cost of free electrons. In the first place, the atm. number of water mol. has been taken to be 10 and the degree of ionisation to be 0.765 ; then the magnetic susceptibility of water has been calcd. and the calcd. value ($-0{,}750\times16^{-6}$) is found to agree fairly well with the observed (-0.720×10^{-6}). In the second place, under the same assumption, the variation of the diamagnetic susceptibility of water due to a rise of temp. is calcd. from the change of density ; the agreement between the observed and calcd. values is also satisfactory, as shown in the table below :-

Temp.	Density	$\chi_{10}/\chi_{2}\,{}_{0}\times10^{6}$ (theor.)	$\chi_{10}/\chi_{2}\,{}_{0}\times10^{6}$ (obs.)
90°	0.9653	1.0272	1.0212
70°	0.9778	1.0169	1.0158
60°	0.9832	1.0123	1.0121
50°	0.9881	1.0083	1.0086
40°	0.9922	1.0050	1.0051
30°	0.9957	1.0020	1.0031
20°	0.9982	1.0000	1.0000
10°	0.9997	0.9987	0.9981
4°	1.0000	0.9984	0.9956

Author

Interchange equilibrium between methylalcohol and heavy hydrogen. G. Okamoto and J. Kwan. *J. Chem. Soc. Japan.* 57, 1179–1189 (1936).–Isotopic partition between hydroxyl group of methyl alcohol vapour and hydrogen gas was detd. by the following expts. with the result $xOH/xH=1.74\pm0.1\%$ where x are atomic percentage of D. 1) About 8% shifted methyl alcohol was shaken with hydrogen in the presence of Pt catalyst to attain an interchange equil, the latter being detd. by analysing the both for deuterium content. 2) Methyliodide derived from the methyl alcohol used was analysed for deuterium content to confirm that only hydrogen atoms in the hydroxyl group were partaking the interchange equil. 3) Shifted methyl alcohol and its vapour at an interchange equil. with the former were separately burned and analysed for deuterium content to find that deuterium was shifted by 10% toward the liquid phase. Combining the obtained result by means of statistical mech. expression of partition equil. with the observed vibrational frequencies of methyl alcohol by Bartholome and Sacchse, it was calcd. that the unknown two frequencies should be associated with isotopic shift, $\Delta\nu=250$–310 cm^{-1} in total, assuming they were high enough to identify the vibrational partition function to unity. Author.

On the size dependency of diamagnetic susceptibility of quartz. Y. Shimizu and N. Takatori. *Sci. Repts. Tohoku Imp. Univ.* **Honda Anniv. Vol.** 306–311 (1936). –The study on the dependency of diamagnetic susceptibility of a substance upon its size has been an atracting subject. In the present investigation, the diamagnetic susceptibility of small grains of quartz was measured in various sizes, which had been obtained by the precipitation method, and detd. with a high magnification microscope. The magnetic measurements were done by the zero method, with an app. of Foëx-Forrer's type improved by Y. Shimizu, one of the authors. The result has shown that the diamagnetic susceptibility of the quartz powder decreases with the diminution of its size, the rate of decreasing with diminishing in its size. Author.

Porality of chemical compounds. IX.

K. Higasi. *Bull. Inst. Phys. Chem. Research*, 15, 776–786 (1936).–The writer believes that the solvent effect on the dipole moment can be interpreted as the induction polarisation of the solvent by the hipole of the solute. In this paper his view was examined by the measurements on the elec. moments of i-propyl and i-butyl alcohol in soln. The results were as follows: i-propyl alcohol 1.706D in C_6H_6 and 1.475D in CS_2, i-butyl alcohol 1.702D in C_6H_6 and 1.414D in CS_2. Furthermore, the moment in soln. of isopropyl ether and pentachlorethane were also explained from the same standpoint. Author.

Number of interchangeable hydrogen atoms in complex salts. G. Okamoto and S. Abe. *J. Chem. Soc. Japan.* 57, 1176–1178 (1936).–To avoid the ambiguity of the atomic fraction ratio in determining the number of interchangeable hydrogen atoms, (n_k), about 100% heavy water was used, making the apparent atomic fraction ratio nearly unity. Four complex salts used were as follows: $[Co(NH_3)_6]_2(SO_4)_3 \cdot 5H_2O$, $[Co(NH_3)_5NO_2]Cl_2$, $[Co(NH_3)_5H_2O]Cl_3$, $[Co(NH_3)_4(Co_3)]Cl$. A known quantity of the sample was dissolved in an excess of 100% heavy water and sepd. from the water after the interchange equil. was established. The quantity of deuterium left behind per mol of the salt was found by washing out all deuterium in the heavy salt with light water and by analysing the latter for deuterium content. These procedure was traced mathematically, and it was found that the lower limits of n_k were fairly close to the stochiometrical upper limit of the salts: all hydrogen atoms in the salts were interchangeable. Author.

Propargation of combustion along the surface of inflammable liquid. V., VI. Effect of winds on the velocity of propagation. T. Kimbara. *Bull. Inst. Phys. Chem. Research.* 15, 871–885. 1090–1104 (1936).–To investigate the effect of winds on the velocity of propagation of combustion along the surface of inflammable liquid, pure alcohol was made to be contained at the bottom of a horizontal pipe, of rectangular cross section, which is closed at its one end with a plate having a small circular opening through which air is to be drawn out while the combustion takes place. Alcohol was kindled at its centre, and the velocities of propagation both along and against the winds were, at the same time, measured photographically. In the case when the temp. of alcohol was between 7°C and 27°C, and the wind velocity in pipe was less than 28cm/sec, the following results were obtained. (1) The velocity of propagation towards the open end (i. e. in unfavorable wind), together with the one towards the closed end (i. e. in favorable wind), decrease as the wind velocity increases. (2) When there is no wind, the velocity towards the open end is greater than what is opposite to this. (3) When the temp. is high, the former velocity remains the greater even when winds are applied. (4) But at low temps., it appears that the former has a tendency to become slightly smaller than the latter. The change of outward appearance of the progressing flame due to winds and the cooling effect of the air stream on the surface of alcohol were also investigated, and some discussions were made with regard to these four expti. results.

Author.

Fluorescence and magnetic susceptibility. T. Takéuchi, T. Inai and K. Inamura. *Sci. Repts. Tohoku Imp. Univ.* **Honda Anniv. Vol.** 312–313 (1936).–Aqueous soln. of aesculin, one of strongly fluorescent substances, is introduced into a capillary tube, whose meniscus is placed in the inhomogenous part of the field between the pole-pieces of a powerful electromagnet of the Nagaoka type excited by a current of 15 amperes. By an impingement of ultra-violet light from a mercury lamp focussed by means of a concave mirror against the surface of soln., a small shift in the equil. position of the meniscus is noted; this indicates an increase in susceptibility of the soln. The maximum displacement observed was about one half of the scale division of the micrometer eye-piece of a telemicroscope. Since any rise in temp. of the soln. occurring in the course

of a single reading due to the exposure to the light must accompany a shift in the opposite direction, and the illumination near the meniscus shows no perceptible effect upon the capillarity action, the shift measured is due chiefly to the change of the susceptibility correlating to the fluorescence. Author.

X-ray interference as seen from a geometrical point of view. M. Marue. *Sci. Repts. Tohoku Imp. Univ.* **Honda Anniv. Vol.** 99–112 (1936)–Interference curves which occur in different methods of X-ray analysis are universally investigated, and an advanced correlation is found between these curves and the mode of existence of atom-plane. For the convenience of analysis the author has allotted a new meaning upon atom-plane. It is considered as a pile of equi-distant parallel planes, instead of single layer, containing multitude of atoms in each layer. Being thus defined and provided with some other devices it plays a new rôle as a geometrical idea, having three degree of freedom-two as direction and one as layer distance. One degree is lowered by Bragg's law and its freedom becomes equal to that of a point upon photographic film. If another condition treads on, the interference spot will be limited on certain curve. All the figures of interference are classified into five types such as azimuth conic, asteriscate, granule circle, zone curve and layer line, of which each is shown to be a modified projection of certain space curve derived from one of five conditions given to the atom-plane. Throughout the course of this work no other method of analysis is taken than those of co-ordinate geometry. Inversion, a kind of transformation, is thought profitable here being used to explain the nature of curves. This work may serve to dispel the perplexity which so gloomily covered this domain of optics. Author.

Studies on the photochemical activation of the oxydation-action of metallic complex salts. A. Watanabe. *Iwata Inst. Plant Biochem.*, 2, 97–128 (1936).–The investigation of the author has been carried out to study the influence of light on the catalytic oxidation of metallic complex salts. The oxidation of potassium iodide, pyrogallol, benzidine, p-phenylendiamine and nadi-reagent and the splitting of hydrogen peroxide by certain metallic complex salts is promoted under the action of ultra-violet and visible light rays. Even those complex salts which exhibit in darkness no oxidative or catalytic activity, were made active photochemically. This action of light is manifested only when the complex salts and substances are illuminated in reaction mixture. The previous illumination of any single component has no influence upon the velocity of reaction. Amongst the rays from the mercury lamp the light of $\lambda=366$ mμ shows the greatest degree of the photochemical action, which is easily understood from the absorption property of the complex salts used. In the case of the oxidation of pyrogallol by complex salts certain accelerating action of infra-red rays was observed. With regard to the relation between the structure of complex salts and the photochemical reactivity, it is noticed that amongst the nitro-cobaltic complexes those which contain two NO_2-groups were most strongly activated by light. The oxidative action croceo-chloride (trans) is more strongly accelerated than that of flavo-chloride (cis). In salts of the type $[Co(NH_3)_5X]$, the coordinatively combined acid groups show influence on the degree of the photochemical activation in the following order: $SCN>NO_2>CO_3>Cl$. As to the mechanism of the observed light action, the author has considered that certain metallic complex salts, through absorption of light energy, become more unstable and increase their tendencies to hydration and hydrolysis, the change which is, according to Shibata's, theory essential for the catalytic actions of these compounds. Author.

Studies on the catalytic action of metallic complex compounds. II. K. Shibata and A. Watanabe. *Iwata Inst. Plant Biochem.* 2, 97 (1936).–The metallic complex salts of different kinds have the power to form indophenole from nadi-reagent. Some complex salts attack selectively certain polyphenols or aromatic amines, which reminds us of the

specific actions of oxidizing enzymes. These selective behaviours probably depend upon the fact, that the substance in question is to be easily coordinated into complex nucleus or not. In the case of the nadirection of metallic complex salts the inhibitory action of substances such as cyanide, hydroxylamine and others manifest itself even in a very dilute soln. The addn. of colloids in the reaction medium enhances noticeably the oxidative action of metallic complex salts on o-and p-polyphenols is delayed by addn. of m-polyphenols, which are able to form complex with metal, but not oxidisable. Benzaldehyde, thioglycolic acid and linoleic acid were also used as substrates for the oxidative action of some metallic salts. The various metallic complex salts act peroxidatic; for example Co(II)-complex and trinitrotriammincobalt oxidise the substances only in the presence of hydrogen peroxide, while many others show in the presence of hydrogen peroxide an extremely strong oxidative action. By the oxidative action of metallic complex salts on various substrates hydrogen peroxide is produced. The addn. of complex salts, which act peroxidatic, as well as natural peroxidase, is thus able to enhance the oxidative action of other metallic complex salts as well as of natural oxidases. Certain complex salts, especially those which act peroxidatic, have more or less the ability to split hydrogen peroxide into water and oxygen. The catalytic as well as peroxidatic activation of hydrogen peroxide occur presumably by coordination of the latter molecule in metal complex nucleus. The frequently observed inhibition of the action of natural catalase by certain metallic complex salts strongly indicate their common reaction mechanism. The velosity of oxidative action of metallic complex salts is dependent on the tension of oxygen. Yet the oxidation of substance can proceed rapidly, even in vacuum or nitrogen atmosphere, when the H-acceptor, such as chinon which can be coordinated in metallic complex, is present. Therefore it is clear that the mechanism of the action of metallic complex salts is the same as that of the so-called dehydrogenases or oxido-reductive enzymes. Author.

Studies on the kinetics of the decomposition of dibromosuccinic acid into monobromofumaric acid in heterogeneous systems. B. Tamamushi and H. Umezawa. *Bull. Chem. Soc. Japan.* **11**, 667–685(1936).–The Kinetics of the following reaction: dl-Dibromosuccinic Acid=Monobromofumaric Acid+Hydrobromic Acid was studied in aqueous soln. both in homogeneous and in heterogeneous Systems, the latter in existence of 1) silica gel, 2) sugarcharcoal, 3) haemin-sugarcharcoal. The expt. in each case was carried out at different temp. namely at 30°, 40°, and 50°C. The reaction on silica gel is monomolecular and it proceeds slightly quicker than the homogeneous reaction, while the reaction on charcoals is more or less retarded and its velocity is given by the equation:

$$\frac{dx}{dt}=\frac{k(a-x)}{1+bx},$$

where a represents the initial concn. of the reacting substance, x the amount of the substance decomposed in time t, and both a and b are consts. It was shown that the results of kinetic measurement can be understood by the adsorption relation of the reacting substance and the reaction products on the catalyst. In the case of silica gel, there is no retarding effect of the reaction products, for these are adsorbed weaker than the reacting substance. On the other hand, in the case of charcoals, the reaction product, monobromofumaric acid, is adsorbed stronger than the reacting substance, and this must be the cause of the retardation. The obtained results are not in disaccordance with Kruyt's theory of molecular orientation in heterogeneous catalysis, but the above mentioned relation in adsorption may have a greater influence on the velocity of the studied reaction. From the measurement of the temp. coeff. of the reaction, the energy of activation was calcd. as follows: E=10925 for the homogeneous reaction, E=10280 for the reaction on silica gel, E=16130 for the reaction on sugar-charcoal and E=10885 cal. for the reaction on haemin-sugar-charcharcoal. Thesr results were explained from the standpoint of Polany-Hinshelwood's theory of the activation energy in heterogeneous reactions.

The intensity of the binding force between adsorbed molecules and catalyst was also taken in consideration in accounting for the reaction-mechanism. Author.

Crystal structure of the aliphatic compound, I-II. Y. Tanaka and R. Kobayashi. *J. Soc. Chem. Ind. Japan.* 39, 411–17 B (1936).–(1) The authors derive the simplest crystal structure among the aliphatic substances, the "paraffin wax lattice" (designated by the authors) from the diamond lattice. The paraffin wax lattice explains the crystallographic and stereochemical properties of the *n*-paraffin hydrocarbon. The quadri-valency of carbon atom and the uni-valency of hydrogen atom in the *n*-paraffin hydrocarbon crystal can not be more clearly illustrated. In the next place, we remark that every carbon atom in the paraffin wax lattice is the centre of a tetrahedron, composed of the adjacent two carbon atoms and two hydrogen atoms. Thus, the carbon atoms in a molecule bind with each other to the direction of 109° 28′. (2) According to the paraffin wax lattice, the main diameters of the *n*-paraffin hydrocarbon molecule, C_nH_{2n+2} are summarised by the following equation, $D=d+d\cdot(n+1)\cdot\sin 109°28'/2=2.797+1.257\ n$ (Å)

Here, D denotes the main diameter, d the diameter of carbon atom (=1.54 Å), and n the number of carbon atoms in a *n*-parffin hydrocarbon molecule. The main diameters, calcd. from the above equation, are equal to the main spacings resulted by the X-ray analysis with regard to the *n*-paraffin hydrocarbon. Thus, it may be naturally assumed that the main spacing of the *n*-paraffin hydrocarbon crystal and the main diameter of the *n*-paraffin hydrocarbon molecule in the paraffin wax lattice are the same in character. (3) Furthermore, the short diameters of the *n*-paraffin hydrocarbon molecules are expressed by the following formulae,

$$D'=h+(d+h)\cdot\sin 109°28'/2=3.18\ (Å)$$
$$D''=h+d\cdot\cos 109°28'/2+(d+h)\cdot\cos 109°28'/2=3.45\ (Å)$$

Here, D' and D'' denote the short diameters and h the diameter of hydrogen atom (=1.06 Å). The short diameters, D' and D'' are constant and independent on the kinds of the *n*-paraffin hydrocarbon. In the same way, the cross-sectional areas of the *n*-paraffin hydrocarbon molecule may be expressed by the following equations,

$$A_a=D\cdot D'=3.18\ (2.797+1.257\ n)\ (Å^2)$$
$$A_b=D'\cdot D''=10.97\ (Å^2)$$
$$A_c=D''\cdot D=3.45\ (2.797+1.257\ n)\ (Å^2)$$

Here, A_a, A_b and A_c denote the cross-sectional areas. It is further shown that the average cross-sectional area of *n*-octane molecule, calcd. from the diffusion coeff. of *n*-octane vapour by Edward Mack, 45.1 Å^2 corresponds to A_c, that is, A_c for *n*-octane molecule $=3.45(1.797+1.257\times 8)=44.3$ Å^2. The agreement is good within the exptl. error. (4) Thus, the volume of the *n*-paraffin hydrocarbon may be illustrated by the following formula, $V=D\cdot D'\cdot D''=10.97\ (2.797+1.257\ n)\times 10^{-24}$ (cc) On the other hand, the equation for mass of the *n*-paraffin hydrocarbon, C_nH_{2n+2}, is

$$M=[19.79n+1.662(2n+2)]\times 10^{-24}=(23.114n+3.324)\times 10^{-24}\ (g).$$

The true density or the density under the stable equil. of the *n*-paraffin hydrocarbon, C_nH_{2n+2}, may be therefore expressed by the following equation,

$$S=M/V=(23.114n+3.324)/(30.76+13.82n).$$

The true density, S refers to the molecular volume V, at which all atoms in the *n*-paraffin hydrocarbon crystal are in stable equil. The corresponding molecular volume at melting point, V' is 1.82~2.02 times as great as V, that is, $V'/V=S/S'=1.82\sim 2.02$ Here, S' represents the specific gravity of *n*- paraffin hydrocarbon at melting point. Thus, the mean atomic spacing of the *n*-paraffin hydrocarbon at melting point is 22~26% greater than the corresponding atomic spacing in stable equil. namely, $(V'/V)^{\frac{1}{3}}=(S/S')^{\frac{1}{3}}=1.22\sim 1.26$. (5) According to the paraffin wax lattice, the volumetric spacing of methyl group in the *n*-paraffin hydrocarbon molecule or distance from the end hydrogen atom of methyl group to the adjacent carbon atom may be easily computed. Good agreement between these computed values and

the side spacings regarding the *n*-paraffin hydrocarbon indicates that the side spacings concern with X-ray absorption of the end methyl group in the *n*-paraffin hydrocarbon molecule. (6) It is clear that the lattice const. or distances between two adjacent atomic rows of the paraffin wax latti e are different from those of the diamond lattice of the same variety. Now, let the lattice spacings, parallel to the 3 axes, be a, b and c (or c') may be calcd. as follows:

$$a=d\cdot\sin 109°28'/2=1.26 \quad (\text{Å})$$

$$b=d\cdot\cos 109°28'/2+(d+h)\cdot\cos 109°28'/2=1.65 \quad (\text{Å})$$

$$c=h=1.06 \quad (\text{Å})$$

$$c'=(d+h)\cdot\sin 109°28'/2=1.06 \quad (\text{Å})$$

Thus, the lattice consts. of the paraffin wax lattice, $a=1.26$ Å, $b=1.65$ Å and $c=c'=1.06$ Å. (7) The resultant force of atomic attractions in a *n*-paraffin hydrocarbon molecule composes, according to the paraffin wax lattice, a force field of rhomb, whose adjacent angles are resp. 109°28′ and 70°32′. The fundamental crystal is therefore of rhombic plate whose neighbouring crystal angles are measured by 109°28′ and 70°32′, and belongs naturally to the ortho-rhombic system, as already reported by the authors. In the fundamental crystal, let the length of main axis be the main diameter, $D(=2.797+1.257\,n)$, then two other crystal axes are resp. equal to $D\cdot\cot 109°28'/2$ and the short diameter $D(=3.18)$. An equation for the axial ratio regarding the fundamental crystal of the *n*-paraffin hydrocarbon is given as follows:

$$a:b:c=D:D\cdot\cot 109°28'/2:3.18=1:0.719:3.18/D.$$

Furthermore, the methane crystal lattice may be assumed to be of the same variety as the original diamond lattice (or a face-centred cube lattice), and b long exceptionally to the cubic system. Author.

2—ATOMIC STRUCTURE, RADIOCHEMISTRY AND PHOTOCHEMISTRY

On the ground state of the hydrogen molecule. T. Nagamiya. *Proc. Phy.-Math. Soc. Japan.* 3, 18, 497–506(1936).–The calcns. of the dissocn. energy and the wave function at the equilibrium distance of nuclei are carried out. The wave function is assumed as a linear combination of functions of the form

$$\psi_l=e^{-\frac{\alpha}{2}(\xi_1+\xi_2)}(\xi_1^0-1)^{\frac{m}{2}}(\xi_2^0-1)^{\frac{m}{2}}\cdot\{\xi_1^{k}\xi_2^{k'}P_l^m(\eta_1)P_{l'}^m(\eta_2)+\xi_2^{k}\xi_1^{k'}P_l^m(\eta_2)P_{l'}^m(\eta_1)\}\cos m(\varphi_1-\varphi_2),$$

(all suffixes and powers are integers and ξ, η are elliptic coordinates), each of which may be interpreted as a rough approxn. for $(1s\sigma)^2$, $1s\sigma 2s\sigma$, $(2p\sigma)^2$, $1s\sigma 3d\sigma$, $(2p\pi)^2$, etc. according as the increasing values of k, l, m. The Ritz-method is used. The calcd. value of the dissocn. energy is 3.94 e. v., being smaller than the exptl. value 4.4 e. v. It is also smaller than the value calcd. theoretically by James and Coolidge. Author.

Elementary calculations on the slowing down of neutrons by a thin plate. H. Yukawa. *Proc. Phys.-Math. Soc. Japan.* 18, 507 (1936).–The energy distribution of neutrons slowed down by a thin plate containing hydrogen, whose thickness is small compared with the mean free path of the incident neutrons of definite energy, is calcd. for following cases, taking only the single and the double scatterings into account. i) Normal incidence: in this case, the distribution function for slow neutrons increases with decreasing energy E as $-\log E$. ii) A point source: in this case, the distribution function is nearly const. iii) A point source and a small detector placed face to face on either side of the plate: in this case also, the distribution function of neutrons, which hit the detector after single scattering, is nearly const.

Author.

On the calculation of atomic energy levels. T. Yamanouchi. *Proc. Phys-Math. Soc. Japan.* **III, 18,** 624 (1936).–The method for finding the energies of an atom or an ion in a specified electron configuration arising from a definite parent term are described in most general manner. For this purpose, the representations of the symmetric group π_n are constructed in the forms reduced for the subgroup π_{n-1}. In most simple cases, however, only the diagonal sums of the representations for the parts occupied by the irreducible representations of π_{n-1} are needed. They are given in simple formulae for the transpositions by utilising the Dirac's identity. The results are compared with the terms of d^n p configurations with satisfactory agreement.

Author.

On the energy states of valency electrons in some metals. I, 1: The crystal energy levels of valency electrons in Zn. M. Satô. *Sci. Repts. Tohoku Imp. Univ.* **Honda Anniv. Vol.** 136 (1936).–From the analysis of L-non-diagram lines α', α'', β', β'' and of Osgood's lines, of Zn, the crystal energy levels of valency electrons in Zn were sought, and 6 levels were detd.; the energy distances from K-level were found to be 710.920, 711.040, 711.280, 711.299, 711.335, and 711.859 in Rydberg unit. In comparison of these values with the curves of K-absorption edges for Zn and for ZnO, due to Barnes, some levels, the existence of which being still in doubt, were detd. Author.

On the energy states of valency electrons in some metals. I, 3: The stationary states of valency electrons in Zn-crystal. M. Satô. *Sci. Repts. Tohoku Imp. Univ.* 25, 771 (1936).–The photoelec. threshold, photoelec. selective emissions and selective absorptions of light, of Zn, have been explained in the terms of the energy levels of the valency electrons that were detd. in the papers already published, and the nature of the so-called potential energy barrier in the surface layer of solid-Zn has thus been clarified. Further, based on the results above obtained and referring to photo-conductive effect it has been concluded that the levels E_3 and E_4 are the conduction levels of the valency electrons and that, in the bulk mass of solid-Zn, the levels, E_1, E_2, E_3 and E_4, at least, are stationary ones. A discussion regarding the origin of the catalytic action in the surface layer of solid-Zn has also been made. Author.

On the Zeeman effect of indium lines $^2P_{\frac{3}{2},\frac{1}{2}}-{}^2S_{\frac{1}{2}}$. ($\lambda\lambda$ 4511 and 4102 Å). Z. Okubo and S. Satô. *Sci. Repts. Tohoku Imp. Univ.* **Honda Anniv. Vol.** 8–27 (1936). –The Zeemam effect of indium lines $^2P_{\frac{3}{2},\frac{1}{2}}-{}^2S_{\frac{1}{2}}$ was studied with a small Lummer-Gehrke plate, in a heterogeous magnetic field. As the deficiency of resolving power of the instrument used and the superimposition of the patterns of the neighbouring orders make it hard to count the numbers of fine components belonging to each grobe Paschen-Back component, the value of the nuclear spin of indium atom has not been absolutely detd. However, it was found that she obtained Zeeman patterns, regarding the variations of the sepns. as well as the intensities of the components with the strengths of the field applied and also the breadths of each grobe Paschen-Back component, are in better agreement with those which are deduced from Goudsmit and Bacher's formula in the case where the nuclear spin is taken as 9/2 than as 1/2. The former value of the spin is the one that has been inferred from the recent investigations on the hyperfine structures of indium lines and the latter is the one that was believed at first for a little while to be probable.

Author.

On the scattering of fast electrons by thin foils of beryllium. H. Saegusa and K. Kikuchi. *Sci. Repts. Tohoku Imp. Univ.* **Honda Anniv. Vol.** 72 (1936).–Total angular distribution of the scattered electrons by a thin foil of beryllium was observed, using two similary made Geiger electron counters and two amplifiers. One of the electron counters was fixed at a scattering angle of 45° and the other is made adjustable within a range of angles from 30° to 110°. The electron

counters were operated concurrently and discharges due to the scattered electron at each angle were recorded both on a same rolled paper. Thus the ratios of the number of the scattered electrons at various angles to that at the fixed angle of 45° were obtained, and from those ratios the angular distribution was calcd. Comparing the values by the present authors and those by Klemperer with the values calcd. from Wentzel's formula, it was found that the authors' agreed better with those of Wentzel than those of Klemperer.

Author.

3—ELECTROCHEMISTRY AND THERMOCHEMISTRY

The electrolytic formation of persulphate. I. R. Matsuda. *Bull. Chem. Soc. Japan*, **11**, 1 (1937), R. Matsuda and T. Nishimori. II *ibid.*, **11**, 750 (1936).–The mech. of the anodic formation of persulphate is studied. K. Elbs and O. Schönherr (*Z. Elektrochem.*, **1**, 417 (1894) attribute its formation to two discharged HSO_4'-ions uniting together. The present authors consider, however, according to their expts. that persulphuric acid is formed by the oxidation of sulphuric acid with the anodic oxygen, and so OH'-ions play an important rôle in this anodic reaction. Electrolyses of (I) sulphuric acid, (II) the same contg. various proportions of ammonium sulphate, and (III) neutral ammonium sulphate soln. are studied over a comparatively wide range of concn. (I) which conts. the least of OH'-ions among the three kinds of soln., when the concn. is the same, has the smallest current efficiency. The more ammonium sulphate the electrolyte conts., the greater the current efficiency : hence the neutral ammonium sulphate soln. which has the greatest concn. of OH'-ions maintains the greatest current efficiency. These facts can possibly explained by the present authors' view, but not by Elbs'. Influences of adding various cations, H^+, K^+, Na^+, NH_4^+, Li^+, Mg^{++}, Zn^{++}, Fe^{+++}, Al^{+++}, Cu^{++}, and Cd^{++}, of disusing diaphragm, and also of viscosity of the electrolyte are considered as well. Author.

On the oxidation equilibrium of Magnesium chloride by water vapour. K. Sano. *J. Chem. Soc. Japan.* **57**, 1019–1024 (1936).–The oxidation equil. of magnesium chloride was investigated by the statical method at the temp. 525°~621° with a specially designed app. consisting of a glass spring manometer and two reaction chambers, each kept in a thermostat having different temps. Magnesium chloride contd. in one of the reaction chambers was oxidized by the water vapour of known pressure produced by dissociation of magnesium chloride hexahydrate in the other, and total pressure of the reaction chamber was measured by the glass spring manometer. From the results obtained, some thermodynamical values of magnesium chloride and the equil. consts. of the reactions $MgO+C+Cl_2=MgCl_2+CO$ and $MgO+CO+Cl_2=MgCl_2+CO_2$ were calcd. Author.

One measuring method of oxidation equilibrium of metal by carbon dioxide. K. Sano. *J. Chem. Soc. Japan.* **57**, 1025–1027 (1936).–A simple device is made in the method of the detn. of oxidation equil. of metals by carbon dioxide and is applied to the reaction $Fe+CO_2=FeO+CO$. The equil. consts. obtained are in good agreement with those of Eastman. Author.

Direct determination of the heat of sorption of water vapour on cellulose with ice calorimeter. S. Oguri and T. Yoshida. *Waseda Appld. Chem. Soc. Bull.* **13**, (4) 1–6 (1936).–In the present study the authors detd. directly the heat of sorption of water vapour on cellulose at 0°C. by means of ice calorimeter. As a sample of cellulose the authors used the standard cotton cellulose prepd. by

the method proposed by the American Chemical Society (Ind. Eng. Chem., 1923, 748). The cellulose sample, which had been dried previously in a desiccator for about twenty days, was placed in a glass tube fixed in the ice calorimeter and was dried thoroughly for 48 hrs. by dry air which was allowed to sweep through the glass tube. The air satd. with water vapour at 0°C. was then introduced into the tube d for 3 minutes so that the sample absorbed the possible amt. of water vapour. The system was then cut off from the air supply and allowed to stand until the wt. of the mercury in the ice calorimeter attained const. To test for possible leakage of heat in the ice calorimeter blank test was carried out under the same condition before the expts. from which it was found that the leakage varied in proportion to time. The obtained heat of sorption for 1 gm of water vapour is 1098 ~915 cal. In the above calcn. the authors assumed that the sample would absorb 19.94 gm of water in the satd. water vapour at 0°C.

Author.

Measurement of the potential of zinc electrode in dry cells, I. G. Fuseya, T. Miyakawa and Y. Akai. *Bull. Toyoda Res. Imp. Invention Soc. Japan.* **4**, 48–64 (1936).–Since it is not yet known how the potential of the zinc electrode changes with the concn. of the soln. or with the temp. the e. m. f. s of the following cells were measured at 0°, 10°, 18°, 25° and 30°, the compn. of the soln. having been varied as shown in Table 1.

$$Zn\,x\,Hg \mid NH_4Cl(Ag) + ZnCl_2(Bg) + H_2O \;(100Og) \mid KCl(sat.) \mid KCl(0.1N),\ HgCl-Hg$$

Table 1. Specific Gravities and P_H of the Solns. used.

Soln. No.	NH_4Cl (mols)	$ZnCl_2$ (mols)	d^{25}_4	P_H
(1)	4.673	0.3668	1.080	4.62
(2)	5.607	0.3668	1.088	4.66
(3)	6.542	0.3668	—	4.70
(4)	4.673	0.7337	1.106	4.56
(5)	5.607	0.7337	1.112	4.60
(6)	6.542	0.7337	—	4.63

The results of the measurement are given in Table 2.

Table 2. The Potential of Zinc Electrode against Decinormal Calomel Electrode.

Soln. No.	10°	18°	30°
(1)	−1.1562	−1.1615	−1.1693
(2)	−1.1651	−1.1710	−1.1796
(3)	−1.1727	−1.1786	−1.1874
(4)	−1.1421	−1.1470	−1.1544
(5)	−1.1514	−1.1565	−1.1642
(6)	−1.1593	−1.1650	−1.1736

The higher the temp. the greater the concn. of NH_4Cl and the less the concn. of $ZnCl_2$, the lower is the potential. Author.

Thermochemical study of inorganic compounds with the non-isothermal adiabatic calorimeter. I. Determination of the integral heat of solution of KCl. Z. Shibata and Y. Terasaki. *J. Chem. Soc. Japan.* **57**, 1208–1211 (1936).–The construction of the non-isothermal adiabatic calorimeter which the authors used, is described and the sensibility was confirmed by the detn. of the integral heat of soln. of KCl. The result is following $Lc\left(=\frac{0.5\ KCl}{100\ H_2O}\right)=-4244\pm5$ cal. The value completely coincided with that of E. Lange and his coworkers. Author.

Thermochemical study of inorganic compounds with the non-isothermal adiabatic calorimeter. II. Detn. of the heat of hydration of $BaCl_2$(s) and the first heat of solution of $BaSO_4$(s). Z. Shibata and Y. Terasaki. *J. Chem. Soc. Japan.* **57**, 1212–1216 (1936).–The heat of soln. of $BaCl_2$(s) and $BaCl_2.2H_2O$(s) were detd. by the non-isothermal adiabatic calorimeter $BaCl_2$(s) : $Lc\left(=\frac{0.1\ BaCl_2}{100\ H_2O}\right)=2845\pm11$ cal. $BaCl_2.2H_2O$(s) : $Lc\left(\frac{0.1\ BaCl_2}{100\ H_2O}\right)=-4367\pm10$ cal. From the above the heat of hydration of $BaCl_2$ was calcd.: $\Delta Q=7212\pm11$ cal. The heat of precipitation of the reaction, $K_2SO_4(aq)+BaCl_2(aq)=BaSO_4(s)+2KCl(aq)$ was detd. using NH_4NO_3 as coagulater and with the heat of dilution of K_2SO_4, $BaCl_2$ and KCl the first heat of soln. of $BaSO_4$ was obtained, $Lo=-5806\pm12$ cal.

Author.

On the equilibrium in the reaction

of fayalite by carbon monoxide. K. Sano. *Kinzoku no Kenkyu.* **13,** 389-393 (1936).-The reduction equil. of fayalite by carbon monoxide was investigated thermodynamically by means of the calcn. of the free energy of the formation of fayalite and ferrous oxide. The reaction of the equil. const. and the tempt. was found as follows: $\log K_p = -988.053/T-3.387\log T+0.000791T-0.00000068T^2+9.377$. Author.

Some thermodynamical values of the transformation of iron and manganese. K. Sano. *Kinzoku no Kenkyu.* **13,** 432-436 (1936).-Some thermodynamical values of the transformations of iron and manganese are calcd. from the exptl. values of heat content obtained by Oberhoffer and Umino. Author.

On the equilibrium state of iron-carbon-nitrogen system. I. M. Kawakami. *Bull. Tokyo Univ. Eng.* **5,** 661-686 (1936).-The free energy of formation of cementite, nitride and cyanide of iron and also of alkali cyanide was calcd. From the observed heat of formation and the heat capacity of iron cyanide prep. the free energy of its formation was obtained. Comparing the free energies, it was found that iron cyanide is an unstable substance, whereas cementite, nitride and alkali cyanides are stable. The stability is attributed to alkali cyanide, cementite and nitride. From these results it was considered that when iron is brought into contact with molten alkali cyanide, cementite and nitride are formed instead of iron cyanide, that is, there occur the cementation and nitriding. When alkali cyanide is left in free air and oxidized, the two reaction may proceed more easily. Author.

A statical method of investigation of the oxidation and reduction equilibrium of iron by water vapour. K. Iwasé and K. Sano. *Sci. Repts. Tohoku Imp. Univ.* **Honda Anniv. Vol.** 465-475 (1936) -The investigation of the oxidation and reduction equil. of metals by water vapour, $3Fe+4H_2O \rightleftarrows Fe_3O_4+4H_2$ and $Fe+H_2O \rightleftarrows FeO+H_2$, is made, using an app. deviced by the writers for the elimination of thermal diffusion effect. The results obtained,

$$(430^\circ\sim552^\circ)\quad \log K_p=\frac{-1,707.5}{T}+1.590 \quad (1/4Fe_3O_4+H_2\rightleftarrows 3/4Fe+H_2O)$$

$$(571^\circ\sim692^\circ)\quad \log K_p=\frac{-654.0}{T}+0.321 \quad (FeO+H_2\rightleftarrows Fe+H_2O),$$

are in fair agreement with those obtained by Kapustinsky, which proves the effectiveness of the new apps. From the values obtained, some thermodynamical values for magnetic and ferrous oxide are calcd. Author.

On the pasted copper electrodes in an alkaline storage cell. T. Tiku. *Bull. Toyoda Res. Imp. Invention Soc. Japan.* **4,** 65-95 (1936).-The auther intended to obtain the pasted positives and negatives of a storage cell, supporting an oxide of a certain metal with the metal grids and transforming the oxide electrolytically into the active materials, from the analogy of the leak and silver accumulators. Expts. showed that copper was favorable for this purpose. In this case the copper grids pasted with cuprous oxide powd. and dilute caustic potash soln. could be transformed into the neg. and pos. plates during the course of electrolysis in the caustic potash soln. The plates thus formed could be submitted to charges and discharges repeatedly. The nature of the discharge characteristic of the positive against an Fe-negative of large capacity was the same as in the case of lead-acid cell and the mean value of terminal voltage was about 1 volt, but the characteristic of the neg. against a nickel-oxide positive of large capacity showed two stages and the first stage was the greater part of the whole discharge and the mean terminal voltages were about 0.8 volt and 0.5 volt resp. in the first and second stages. The capacities of the negatives amounted to about 0.2-0.3 amp. hr. per 1 gram of the paste, while only less than the one-twentieth of that value was obtained for the positives. In above cases, the current density was 1×10^{-2} amp./cm^2. In the course of discharge of the negatives the gradual change of colour of active material from dark

red-brown to green-yellow were observed. For the negatives, the linear relation was found between the mean discharge capacities during several cycles at the same current and the logarithms of that current values. And in the case of charge or the formation of the negatives, generation of hydrogen gas bubbles was not at all observed until the charged capacity amtd. to definite values and so the time when the gassing began was clearly detd. The elec. efficiencies were about 60%, forthe pos. and neg. plates. Author.

Evuivalent conductivity of 1-1 salts. S. Kaneko: *J. Chem. Soc. Japan*, **57**, 1320–1323 (1936).–Concerning the equiv. conductivity of 1–1 salts the following equations are derived from the theory of the former report [loc. cit. **56**, 1320 (1935)]

$$\Lambda=\Lambda_0-(\alpha\Lambda_0+\beta)\sqrt{C}+AC.$$

$$\alpha=\frac{1}{3}\left(1-\sqrt{\frac{1}{2}}\right)B_1\,B_2^{1/2}.\quad \beta=B^{1/2}B_3.$$

$$A=\frac{1}{12}B_1B_2\Lambda_0\alpha+B_2B_3\sum_{\nu=0}^{\infty}\frac{B_1^{2\nu}\alpha^{-2\nu+1}}{(2\nu+1)!(2\nu-1)},$$

$$B_1=\frac{\varepsilon^2}{DkT}.\quad B_2=\frac{8\pi N\varepsilon^2}{1000\,DkT}\quad B_3=\frac{N\varepsilon^2}{3\pi\eta}\times\frac{10^{-11}}{9}.$$

where Λ is equiv. conductivity; Λ_0 equiv. conductivity at infinite dilution; C, concn. of the soln.; D, dielectric const. of the solvent; k, Boltzmann's const.; T, absolute temp. ε, charge of anelectron; N, avogadro number; η viscosity of the solvent; a diameter of ions. Author.

Measurement of the thermal diffusion effect in the mixture of hydrogen and water vapor. Z. Shibata and H. Kitagawa. *J. Chem. Soc. Japan.* **55**, 722–735 (1935). **57**, 1300–08. (1936).–Using app. with Pt-(at higher temp.) and Pd-semipermeable membrane (at lower temp.) designed by authors, the resulting pressure difference of hydrogen by the thermal diffusion effect, hydrogen pressure at cold part, total pressure, and water vapor pressure at cold part, which was kept at const. vapor pressure, were measured, and then $(P_{H_2O})_{\text{hot part}}$ was calcd.; the one end of the vessel containing the mixtures of hydrogen and water vapor of any compn. was heated between 201~102.1°, and the other at room temp. The results show the linear relation between $\log\left(\frac{P_{H_2O}}{P_{H_2}}\right)_{\text{hot part}}$ and $\log\left(\frac{P_{H_2O}}{P_{H_2}}\right)_{\text{cold part}}$, nearly symmetrical curve having max. at 50–60% H_2 for $\Delta\lambda$ -Compn. and that $\Delta\lambda$-$\log\left(\frac{T_1}{T_2}\right)$ are the straight line passing the origin at lower temp. and curve at 500–700° gradually. According to Chapman's theory the rigidity of both molecules and the index of repulsive force are calcd. The rigidity of both molecules are 0.40 at lower temp., nearly one at higher temp. The index of repulsive force is 6~7 at lower temp., 9~11 at higher temp. Author.

Vapour pressure determination of solid mercuric hologenides. Z. Shibata and K. Niwa. *J. Chem. Soc. Japan.* **57**, 1309–1319 (1936).–The Vapour pressures of solid $HgCl_2$, $HgBr_2$ and HgI_2 (red) were detd. by the effusion method at the temp. between 50 and 90°C. The microblance, hanging the quarz crucible which had an orfice in the lid, was situated in the vacuum of 10^{-5} mm Hg at the required temp. The effusion velocity of the satd. vapour of the sample from the orfice was detd. with the rider, which had been formerly weighed, and a stopwatch exactly. The vapour pressure of solid halogenides were calcd. from these effusion velocity and the area of the orfice which had been detd. by a microscope, drawing app. and planimeter. From the vapour pressures of Benzophenone, $HgCl_2$, $HgBr_2$ and HgI_2 (red), thus detd., we calcd. the heat content of sublimation, free energy-change, and entropy change etc., and the moleculor energy were calcd. from these heats of sublimation and lattice energies which had been calcd. by us. Finally, we discussed the limits of these detn. Author.

On the chemical property of surface of silver. N. Kameyama and S. Kikuchi. *J. Soc. Chem. Ind. Japan.* **40**, 38–39 (1936). –A very thin film of silver was prepd. on a glass plate by means of the vacuum evaporation. The silver film thus pred. did not change

its colour and lustre, when immersed in water. But when immersed in the normal soln. of KCl, it changed its colour from violet into whitish, and its lustre from brilliant metallic into matt; when immersed in the normal soln. of KBr, it changed into goldish colour. And this was done in the hydrogen atm. absolutely freed from oxygen. The above expt. showed that silver in the surface seemed to have turned into silver halide, while silver in the inner part persisted without reaction. Almost all the literatures show that silver is so stable that it is not attacked in the halide soln. in absence of oxygen. Also it cannot be otherwise from thermodynamical consideration based upon the calcn. of the free energy change of the reactions. The reaction is supposed as follows:

$$Ag_{(s)} + Cl^- + H_2O = AgCl_{(s)} + OH^- + 1/2\,H_2$$

Initial system Final system

The free energy per one gramatom of Ag is F in initial system, F′ in final system. In calcg. the difference of the free energies per one gram atom of Ag.

$$-\Delta F = F - F' = -24{,}643 - 1364.9 \log A_{OH^-}$$

(in calorie & at 25°C)

In this equation, if $-\Delta F$ be >0 the reaction is possible. And the possibility depends only on A_{OH^-}, activity of hydroxyl ion, as seen from the above equation. In order to see the effect of A_{OH^-}, we repeated the expt. with KCl & KBr solns. made 0.002N with regards to NaOH, in the hydrogen atm., absolutely freed from oxygen. The result was just the same as above described. Thus the literatures & calcn. deny that the ordinary solid silver reacts with the halide solns. Therefore, we came to the conclusion from our expts. that the silver in tne surface acts in the different manner from the inner silver, and we expect also that this fact may give some hints to the theory of the photographic latent image. Because the latent image is supposed to-day the aggregation of a few silver atoms, the surface of which is important in the development.

Author.

4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY

On electrophoresis, electroendosmosis, viscosity and ζ-potential of suspension of Japanese acid clay. K. Yamamoto. *Waseda Appld. Chem. Soc. Bull.* **13**, (4) 18–29 (1936).–Velocities of electrophoresis and electroendosmosis of water suspension of Japanese acid clay have been detd. and electrokinetic potential or ζ-potential of Japanese acid clay has been obtained. As comparison, the same experiences have been conducted on Fuller's earth, kaolin, silica gel, ferric hydroxide gel and colloidal carbon etc. Author.

On the sorption of chlorine by active charcoal. 1 Relation between the sorption amounts, the temperature, and the pressure. K. Arii. *Bull. Ins. Phys. Chem. Research.* **15**, 1233–1244 (1936).–The sorption of chlorine by active sugar charcoal has been detd. by a static method. The instrument used for the measurements was an all-glass app. which contains Jackson's glass-spring manometer and McBain's quartz-spring balance. The following results have been obtained. The sorption isotherms have been detd. at 20°, 30°, and 50° over a range of pressure below one atm. The results obtained are in good agreement with Langmuir's equation: $a = \frac{\alpha\beta p}{1+\alpha p}$. The following empirical equations hold for the isostere (relation between the equil. pressure and the temp. at the const. amt. sorbed) and the isobar (relation between the amt. sorbed and the temp. at the const. equil. pressure) resp.: $\log p = A - \frac{B}{T}$, and $a = a_0 - Kt$. In the equations, a is the sorption amt. expressed in mg. per 1 g. charcoal, p the equil. pressure in cm Hg, T the absolute temp. and A, B, α, β, and K are the consts. Thus the general equation between a (mg), p (cm), and

t (°C) can be expressed as follows: $a=a_0-\left(k+\frac{n}{p}\right)t$, where k=0.091 and n=12.00. The differential isosteric heats of sorption have also been calcd. Author.

Thermal analysis of the catalytic actions of colloids. (I) Catalytic decomposition of hydrogen peroxide by colloidal platinum. E. Suito. *Rev. Phys. Chem.* **10**, 251–270 (1936).–The reaction was studied by means of thermal analysis of reaction velocity. In a glass calorimeter, dil. H_2O_2 solns. (ca. 0.03M) were decomposed by Pt-sols ($5\sim15\times10^{-6}$ gm. atom) prepared by Bredig's method, at 30°C. From the change of temp. in the reaction system, the reaction velocity was calcd. The reaction proceeded consecutively in two stages. The reaction type in the *earlier* stage could not be detd. The duration of this stage was not influenced by the concn. of H_2O_2 solns., while the larger the amount of the colloid the shorter it became. The *later* stage, the main part of the reaction, was exactly of the first order with respect to H_2O_2, and its velocity const. was almost proportional to the second power of the amount of the colloid. The activity of the colloid changed with time, at first it increased. The heat of the decompn. of H_2O_2 was 23.9±0.5 Cals. per gm. mol as mean value of 22 expts. Author.